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(54) POLY(ARYLENE SULFIDE) RESINS

(71) We, PHILLIPS PETROLEUM COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Bartlesville, Oklahoma, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to stabilized poly(arylene sulfide) resins. In one aspect, it relates to poly(arylene sulfide) resins treated with organo-phosphinic acids to inhibit discoloration. In another aspect, it relates to poly(arylene sulfide) resins treated with organic phosphites to inhibit discoloration. In another aspect, it relates to poly(phenylene sulfide) resins resistant to heat-induced discoloration by virtue of treatment with organo-phosphinic acids or organic phosphites.

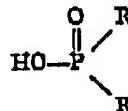
Poly(arylene sulfides) which have not been subjected to elevated temperatures, and which do not contain groups capable of imparting color to the polymers are generally white or light colored. However, during high temperature curing, molding, or other heat treatment, the polymers often undergo considerable darkening. This darkening occurs even though air is excluded during the high temperature treatment. For example, although poly(p-phenylene sulfide) does not discolor when subjected to temperatures up to about 290°C for one hour in a sealed, evacuated container, the polymer does become gray-brown when heated at 365°C under the same conditions. Since it is frequently desirable to cure these polymers at temperatures as high as 425°C, this curing will result in an undesirable coloration of white or nearly white polymers. The term "curing" as used herein refers to heat treatment of the polymers wherein the molecular weight of the polymer is thus increased.

Furthermore, even cured polymers, i.e., polymers whose molecular weight has been increased by heating and which have been discolored thereby, which are subjected to later heat treatment for the purpose of molding or

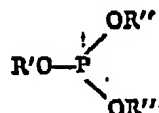
coating, will undergo even further discoloration. This discoloration is aesthetically undesirable, and limits the application of these resins in certain specific instances.

It is known to inhibit the discoloration of poly(arylene sulfide) resins by the addition thereto of a monothiol or polythiol as disclosed in U.S. Patent 3,386,950. It is also known that the discoloration of poly(arylene sulfide) resins can be inhibited by the addition of a hydroxy-substituted amine as disclosed in U.S. Patent 3,408,342.

In accordance with this invention, it has been found that certain organophosphinic acids and organic phosphites inhibit discoloration of poly(arylene sulfide) resins. The organo-phosphinic acids and organic phosphites used in accordance with the invention are of the formulae



and



respectively, where one of the R groups is aryl and the other is hydrogen or aryl;

R' is an alkyl, aryl, cycloalkyl, alkaryl or aralkyl group containing up to 20 carbon atoms; and

R'' and R''' are each hydrogen or a group as defined for R'.

In the formula of the organophosphinic acids, the aryl group(s) represented by R or by both R's, as the case may be, may be monocyclic or polycyclic, but preferably contain no more than 3 rings. Typical values include phenyl, tolyl, ethylphenyl, butylphenyl, propyltolyl, ethylhexylphenyl, naphthyl, anthryl, and phenanthryl.

[Price 25p]

The term "arylene sulfide polymer" as used in this specification is intended to include polymers of the type which are prepared as described in U.S. Patent 3,354,129. As disclosed in this patent, these polymers can be prepared by reacting a polyhalo-substituted cyclic compound containing unsaturation between adjacent ring atoms and an alkali metal sulfide in a polar organic compound. The resulting polymer contains the cyclic structure of the polyhalo-substituted compound coupled in repeating units through a sulfur atom. The polymers which are preferred for use in this invention, because of their high thermal stability and availability of the materials from which they are prepared, are those polymers having the repeating unit —R—S— where R is phenylene, biphenylene, naphthylene, biphenylene ether or a lower alkyl-substituted derivative thereof. By "lower alkyl" is meant alkyl groups having 1 to 6 carbon atoms such as methyl, propyl, isobutyl and n-hexyl. The preparation of such polymers is quite well disclosed in the above patent of Edmonds et al.

The polymers of this invention are preferably those which have melting temperatures above about 204°C. These arylene sulfide polymers can have a melting temperature anywhere in the range from 204°C. to 482°C. Polymers of phenylene sulfide normally have melting temperatures in the range from about 288 to 482°C. The preferred polymers have an inherent viscosity in chloronaphthalene at 206°C. of at least 0.1, more preferably between 0.1 and 0.3 and ideally between 0.13 and 0.23.

The invention is broadly applicable to polyarylene sulfides formed by any technique. It can be used, for example, with the resins manufactured as described in U.S. Patent 2,513,188 prepared by reacting mixtures of p - dichlorobenzene and 1,2,4 - trichlorobenzene with sulfur and a metal halide at fusion temperatures. It can also be used with resins manufactured by the method described in British Patent 962,941 wherein metal salts of halothiophenols are heated at a polymerizing temperature. The invention is especially useful with polymers produced by reacting anhydrous sodium sulfides with polyhalo-substituted cyclic compounds in polar organic solvents as disclosed in U.S. 3,354,129. The invention can be used with linear polymers formed by use of dihalo aromatic compounds or with crosslinked polymers wherein polyhalo aromatic compounds are added to the polymer to aid crosslinking.

Representative examples of organophosphinic acid that can be employed include phenylphosphinic acid, diphenylphosphinic acid, phenyl(1 - naphthyl)phosphinic acid, 8 - anthrylphosphinic acid, di(3 - phenanthryl)phosphinic acid, 4 - eicosylphenylphosphinic

acid and di(2,4,6 - triethylphenyl)phosphinic acid.

The amounts of the organophosphinic acids utilized in the polyphenylene sulfide are preferably from 0.01 to 20.0 parts by weight per 100 parts of the polymer. A more preferred range is from 0.25 to 3.0 parts acid per 100 parts polymer.

Typical examples of organic phosphites that can be employed include isobutyl phosphite, ethyl phosphite, cyclohexyl phosphite, phenyl phosphite, tridecyl phosphite, cicosyl phosphite, 1 - naphthyl phosphite, 2 - phenanthryl phosphite, 1 - (3,5,7 - triethylanthryl) phosphite, di(2 - phenylethyl) phosphite, di(hexadecyl) phosphite, dicyclopentyl phosphite, dioctyl phosphite, diethyl phosphite, di(tridecyl) phosphite, dibutyl phosphite, diphenyl phosphite, didecyl phosphite, cyclohexyldecylphenyl phosphite, trioctyl phosphite, trimethyl phosphite, triethyl phosphite, tributyl phosphite, triisobutyl phosphite, tri(sec - butyl) phosphite, tri(tert - butyl) phosphite, trihexyl phosphite, tricyclohexyl phosphite, tri(2 - ethylhexyl) phosphite, triisooctyl phosphite, tri(tridecyl) phosphite, tri(heptadecyl) phosphite, tri(octadecyl) phosphite, tricosyl phosphite, phenyldidecyl phosphite, phenyldi(hexadecyl) phosphite, phenyldi(nonadecyl) phosphite, diphenyldecyl phosphite, diphenylheptadecyl phosphite, diphenylnonadecyl phosphite, triphenyl phosphite, tri(p - octylphenyl) phosphite, tri(1 - naphthyl) phosphite, tri(2 - naphthyl) phosphite, tri(p - dodecylphenyl) phosphite, and tri(nonylphenyl) phosphite.

Particularly suitable phosphites are di- or trioctyl phosphite, diethyl phosphite, dibutyl phosphite, diphenyl phosphite, and di- or tridecyl phosphite. Of these, dioctyl phosphite is presently preferred.

The amounts of the organic phosphites utilized in the poly(arylene sulfide) resin are preferably from 0.01 to 20 parts by weight per 100 parts of the polymer. A more preferred range is from 0.25 to 3 parts organic phosphite per 100 parts polymer.

The organophosphinic acid or organic phosphite can be incorporated in the polymer prior to heat treatment in any convenient manner. For example, the organophosphinic acid or organic phosphite can be added as such to the polymer and the resulting mixture can be agitated in any suitable manner to achieve good mixing.

The stabilizing acid can be added to the polymer in several ways. For example, the acid can be dissolved in a suitable solvent such as acetone, or methanol-water. The solution is sprayed on the polymer or slurried with the polymer to distribute the additive. If desired, the treated polymer is given additional mixing in a tumble blender or Henschel mixer, to more thoroughly distribute the additive. The mixing devices mentioned can also be used to blend the powdered acid with the

polymer powder. It is also feasible to incorporate the stabilizer in molten resin by using a Banbury mixer, Brabender mixer or extruder.

5 It is also within the scope of the invention to admix the polymer and color stabilizing phosphorus compound with suitable plasticizing agents, dyes, fillers, and pigments.

10 Heat treatment of the polymer and color stabilizers of the invention can be accomplished by incorporating the phosphorus additive into the polymer and then subjecting the polymer-containing additive to a curing temperature such as an elevated temperature in the range 150–400°C, preferably 200–370°C, for a period of one hour to 24 hours, preferably three hours to twelve hours.

20 The compositions of the invention can be used as coatings on various substrates such as metals and ceramics. The compositions are suitable for preparing many useful articles by injection molding, extrusion and compression molding techniques. Such articles include profiles, mechanical parts, and containers.

Specific Example

Color stabilizing additives of the invention were melt blended (one per cent by weight) with polyphenylene sulfide for ten minutes under a nitrogen blanket in a Brabender mixer at a temperature of about 290°C. The control was similarly treated. A film, 5 mils thick, was compression molded from each of the samples at about 330°C under a pressure of 30,000 psig for 30 minutes and then cooled rapidly. The color of each film was visually evaluated according to the Gray Scale for Staining Test devised by the American Association of Textile Chemists and Colorists (AATCC). In this test a gray color is compared with a white standard. A rating of 1 indicates that a sample has changed in color from white to about black. A rating 5 indicates no change from the white standard. The results are presented in Table I.

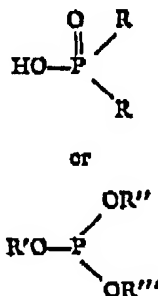
TABLE I

Additive used	Gray Scale rating
none (control)	1.5
phenylphosphinic acid	3.5
dioctyl phosphite	2.0

50 These data show that the color of polyphenylene sulfide resin subjected to elevated temperatures during melting and molding are reduced by incorporating such additives into the resin prior to the heat treatment. The formulations of Table I containing the additives are suitable for coating applications.

WHAT WE CLAIM IS:—

1. A method of stabilizing poly(arylene sulfide) resin compositions against discoloration which comprises incorporating therein an organic phosphorus compound of the formula: 60



where one of the R groups is aryl and the other is hydrogen, or aryl; 70

R' is an alkyl, aryl, cycloalkyl, alkaryl or aralkyl group containing up to 20 carbon atoms; and

R'' and R''' are each hydrogen or a group as defined for R'. 75

2. A method according to claim 1, wherein the organic phosphorus compound is incorporated in an amount of from 0.01 to 20 parts by weight per 100 parts of poly(arylene sulfide). 80

3. A method according to claim 2, wherein said amount is from 0.25 to 3.0 parts by weight per 100 parts of poly(arylene sulfide).

4. A method according to claim 1 or 2, wherein the organic phosphorus compound is dioctyl phosphite or phenylphosphinic acid. 85

5. A method according to any one of claims 1–4, wherein the poly(arylene sulfide) has a melting point in the range 204 to 482°C. 90

6. A method according to any one of claims 1–5, wherein the poly(arylene sulfide) has an inherent viscosity in chloronaphthalene at 206°C in the range 0.1 to 0.3. 95

7. A method according to claim 6, wherein the inherent viscosity is in the range 0.13 to 0.23.

8. A method according to any one of claims 1–7, wherein the poly(arylene sulfide) is a poly(phenylene sulfide). 100

9. Poly(arylene sulfide) resin compositions when stabilized against decoloration by a method claimed in any one of claims 1–8. 105

10. Poly(arylene sulfide) resin compositions according to claim 9, which have been cured by heating the composition after incorporation of the stabilizer.

For the Applicants,
D. YOUNG & CO.,
Chartered Patent Agents,
9 Staple Inn,
London, W.C.1.

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